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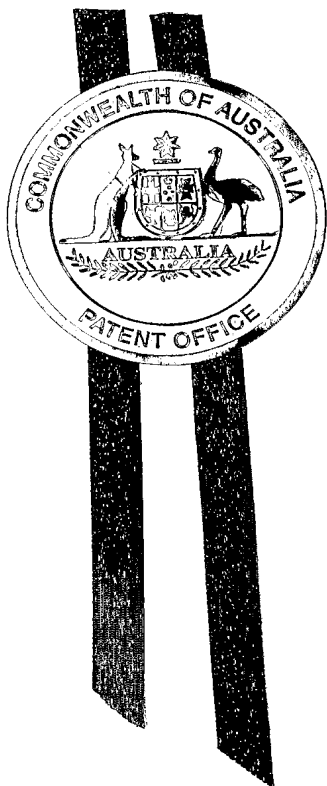


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I, LEANNE MYNOTT, MANAGER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003907176 for a patent by THE AUSTRALIAN NATIONAL UNIVERSITY as filed on 23 December 2003.



WITNESS my hand this
Thirteenth day of January 2005

A handwritten signature in dark ink, appearing to be 'LM' or 'Leanne Mynott'.

LEANNE MYNOTT
MANAGER EXAMINATION SUPPORT
AND SALES

A U S T R A L I A

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Water-Based Cleaning"

The invention is described in the following statement:

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WATER-BASED CLEANING

Technical Field

- 5 The present invention relates to the cleaning of articles and surfaces, and is particularly concerned with cleaning using water.

Background

- 10 The fundamental reason why oil molecules do not dissolve in water is because hydrocarbon (and fluorocarbon) molecules are non-polar and so cannot replace the strong water-water bonds, which need to be broken to incorporate the solute molecule, with equally strong water-solute bonds. For hydrocarbon molecules to be dissolved in water, the water molecules have to be forced apart so that they can then form ice-like
15 clusters around the hydrocarbon. The larger the hydrocarbon molecule, the more water molecules need to be disrupted, and so the lower the solubility. For example, heptane is slightly soluble in water but the larger molecule dodecane is almost completely insoluble. Because this disruption of water is unfavoured, hydrocarbon molecules in water will experience a short-range attractive force, caused by the
20 favoured release of any disrupted water molecules back into their bulk state. Hydrocarbon molecules are, therefore, forced together and 'bond' in water. This bond is called the hydrophobic bond (1). The same factors explain why polar materials, such as sugars, alcohol and salts, are readily soluble in water, since these solutes interact favourably with the surrounding water molecules.

- 25 However, molecular solutions are not the only method for mixing phases. In nature many insoluble materials are 'dispersed' in water in a finely divided state, as a colloidal solution, such as biological cells in blood, clay particles in river water and oil/water emulsions. In each case, microscopic particles of one phase are stabilized in
30 water, usually by repulsive electrostatic forces, which can overcome the ubiquitous attractive van der Waals force (2). Over twenty years ago another important attractive

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force was discovered, acting between hydrophobic particles in water. This force was called the hydrophobic interaction (3). The unexpected strength and range of this force has made a proper theoretical explanation difficult, although it is well accepted that this force is the major cause of instability of hydrophobic colloids in water (4). In the last few years experimental studies have provided evidence in support of an explanation related to the presence of dissolved gas in water (4,5,6). Even in some early studies (7) there was experimental evidence for the formation of vapour- or gas-filled bridges created as two hydrophobic surfaces were separated in water. Further evidence for this effect was obtained last year in a study of the effect of complete de-gassing on the dispersion of oil droplets (and hydrophobic solids) in water (8). De-gassing appears to facilitate the dispersion of oils and finely divided hydrophobic solids, without the need for common dispersants, such as polymers and surfactants.

Water-based cleaning is effective because hydrophilic, polar solutes, such as sugar and salt (ie 'dirt') dissolve readily in water, which is a good general purpose solvent. However, hydrophobic dirt, such as charcoal, grease and oil, is not water soluble at normal temperatures. To overcome this problem, these materials are dispersed in water via a combination of mechanical agitation (during conventional washing) and by the use of added surface active solutes, such as soaps or detergents (surfactants), which coat hydrophobic materials in water. Surfactant molecules adsorb onto hydrophobic surfaces in water, making them hydrophilic which enhances dispersion (not solubility) in water, so that they can be carried away in the aqueous phase during cleaning. Liquid hydrocarbon oils can also be absorbed into micelles formed by these surfactants, facilitating cleaning.

25

Summary of the Invention

It would be highly advantageous to be able to remove hydrophobic dirt from articles and surfaces using water without any or with reduced amounts of surfactants and other dispersants.

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According to the present invention, there is provided a method of cleaning an article or surface with water, which comprises applying de-gassed water to the article or surface whereby dirt on the article or surface disperses or dissolves in the water.

- 5 Also according to the present invention, there is provided apparatus for cleaning an article or surface with water, which comprises means for degassing the water and means for applying the de-gassed water to the article or surface whereby dirt on the article or surface disperses or dissolves in water.
- 10 The relatively low level of dissolved gas present in water at room temperature, of about 1mM (or 20mL of gas per litre) suggests that its influence should be limited to processes involving relatively low (hydrophobic) surface areas. For micellar (9) solutions and microemulsions (10), the number of dissolved gas molecules is small relative to the interfacial area available per unit volume of mixture, de-gassing
- 15 appears not to influence the properties of these systems.

By comparison, the breakaway of oil droplets from a macroscopic oil/water interface, and the dispersion of finely divided hydrophobic particles, offers a low surface area process which can be influenced by a reduction of this relatively low level of

20 dissolved gas. This is even more the case when dissolved gas molecules accumulate next to oil-water (and hydrophobic particle/water) interfaces. This is believed to be because dissolved oxygen and nitrogen (dissolved carbon dioxide is at the much lower level of about 10 μ M) molecules, like hydrocarbons, will disrupt adjacent water molecules because of their non-polar nature and weak van der Waals interaction with

25 water. The presence of macroscopic, hydrophobic surfaces ought to attract these dissolved gas molecules from the water phase and this accumulation may also be aided by the increased gas solubility in hydrocarbon oils, which can be an order of magnitude higher than water. The presence of this layer of dissolved gas, in a thin film, which is placed under a negative (suction) pressure during droplet/particle

30 breakaway, may cause gas cavities to nucleate, which will oppose droplet release. The precise detail of this process is not known but it may be related to cavity bridging, or

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an enhanced van der Waals attraction, between the surfaces, across the gas phase. Whatever the mechanism, reducing the amount of dissolved gas in the water has been found to reduce the forces holding the oil and other hydrophobic particles (eg oil, grease and charcoal, and herein separately or together referred to as "hydrophobic dirt") to the article or surface and to allow the hydrophobic dirt to be released into the water.

Using de-gassed water to aid in the dispersive removal of hydrophobic (solid or liquid) dirt represents an entirely different approach compared to cleaning with detergents. The main detergent action is to coat hydrophobic surfaces to make them hydrophilic, and hence readily dispersible in water. However, in both cases the crucial step will involve the separation of two surfaces from intimate molecular contact and the exposure of a least one hydrophobic surface to water. This will occur even in the presence of detergent, just prior to its adsorption. Simple thermodynamic arguments predict that the separation of one or two hydrophobic surfaces in water is expected to produce cavitation between the surfaces. This cavitation acts to prevent the separation, and hence removal of dirt, both because of the energy needed to vaporise water and the strong, short-range van der Waals force generated between two materials across a vapour phase.

20

In detergent cleaning, hydrophobic materials usually become charged due to detergent adsorption and this helps to stabilise them. However, it has recently been demonstrated that hydrophobic colloids naturally develop a significant charge in water which also helps stabilise them in water (11). In detergent cleaning, the surfactant-coated hydrophobic dirt is thermodynamically more stable in water than hydrophobic dirt dispersed under de-gassed conditions. However, we have demonstrated that, although not thermodynamically stable in water, hydrocarbon oil droplets, dispersed using de-gassed conditions, do not coalesce and remain in a meta-stable state of more than sufficient duration to be effective in cleaning.

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By "applying the de-gassed water" as used herein is meant any arrangement by which the de-gassed water can be caused to act on the article or surface in the method or apparatus of the invention. This includes introducing an article to a container of the de-gassed water in which the article may be left for a period of time to "soak", with or
5 without agitation. It also includes spraying or blasting the article or surface with the de-gassed water, preferably using an airless pump, and merely causing the de-gassed water to relatively flow over the article or surface.

The invention described herein is therefore analogous in some respects to normal
10 cleaning, except that the dispersion of hydrophobic dirt is achieved at least primarily by the use of de-gassed water. The dispersion of hydrophobic dirt, including the time taken for the cleaning, is advantageously enhanced by the use of mechanical action combined with de-gassed water. This mechanical action can be in the form of, for example, jets of de-gassed water, preferably fine jets, directed onto a dirty article or
15 surface, or any conventional mechanical action. Mechanical action combined with the dispersive power of de-gassed water will disperse hydrophobic dirt, while hydrophilic, polar, dirt (eg salts, sugars) will be dissolved in the normal manner. Thus, soluble dirt is dissolved, while hydrophobic dirt is dispersed and all of the dirt may then be rinsed away. Long term stability of the dispersion of dirt in water is not
20 required in cleaning, and subsequent de-stabilisation could actually be useful. However, as with conventional cleaning, the addition of hydrophilic, polymeric stabilisers, such as sodium carboxymethylcellulose, may also be used to enhance the longer term dispersive power of de-gassed water, preventing the re-deposition of the dirt.

25 By "de-gassed water" is meant that at least 90%, preferably at least 97%, of the dissolved gases that are present in the source water are removed. The cleaning action of the de-gassed water will be enhanced at higher levels of de-gassing, and more preferably at least about 99.99%, most preferably about 99.999%, of the dissolved
30 gases are removed from the source water. The source water may be distilled water, tap water or, for some purposes, even recycled cleaning water.

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The de-gassing of the water can be achieved by any suitable vacuum pump with a nitrogen trap. In one embodiment, de-gassing is achieved by repeated freezing and pumping using an efficient mechanical pump. Once the space above the frozen water
5 was out-gassed, to typically better than a mTorr, a Teflon tap was closed and the water warmed to room temperature so that remaining dissolved gases were pulled into the space above the liquid. This may be repeated, for example, up to four or five times to ensure almost complete removal of the dissolved gas. When connected to a separate vacuum line, of substantially greater volume, the mechanical pump achieved
10 pressures down to 20 – 40 μ Torr. Evacuation of the water to lower than a mTorr corresponds to greater than 99.999% removal of the dissolved gas. Evacuation of the water to lower than about 20 Torr corresponds to greater than about 97% removal of dissolved gas, and evacuation of the water to lower than about 20 milliTorr corresponds to greater than about 99.99% removal of dissolved gas.

15 The cleaning may be performed at any temperature between (not including) 0°C and 100°C, but is conveniently performed at room or ambient temperature.

The potential advantages of a detergent-free cleaning system are enormous in terms of
20 cost and environmental savings, and might be of particular value for specialist applications. Some examples follow.

Micro-electronic circuits currently have to be cleaned with relatively toxic solvents that are expensive and have to be recycled. De-gassed water can be sprayed onto
25 delicate electronic devices without the disadvantage of leaving residual detergent coatings. The washings can be discarded.

Automobile surfaces, and other surfaces, may be cleaned using a tube held close to the contours of the surface and moved across the surface. Holes in the tube produce
30 fine jets of de-gassed water, which hit the surface and clean via dissolution and dispersion.

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Household clothes' washing systems may be developed using agitation of clothes in a basin with fine jets of de-gassed water covering all articles of clothing over the period of agitation. Clothes and other articles may also be left to soak in a container of de-gassed water optionally with agitation of the articles.

Vegetables are often cleaned using a water-based flotation process. De-gassed spraying could offer a detergent-free alternative.

The rate of diffusion of air into de-gassed water is remarkably slow and so should not present a problem for spray processes, where the de-gassed water is exposed to air for only a brief length of time (ie. seconds). Theoretically, at room temperature it takes about 10 days to reach dissolved gas saturation to a depth of 1cm in quiescent, de-gassed water. However, external factors, including vibration and convection, may accelerate the diffusion process.

Brief Description of the Drawings

Aspects of the present invention will now be described in detail, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is graph showing percentage of de-gassing against vacuum pressure in a mechanical pump with a liquid nitrogen trap;

Figures 2a and 2b are photographs showing samples as described in Example 1; and

Figure 3 is a graph illustrating the turbidity of normal gassed water and of de-gassed water after shaking in a container contaminated with dodecane as described in Example 2.

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Figure 1 illustrates the vacuum required for a degree of de-gassing between 99.87% and 99.999%, if it is assumed that the final pressure achieved on several cycles of freeze/thaw/pumping is given by the pressure in equilibrium with the final frozen liquid, which on being melted does not give any visible bubbling/out-gassing.

5

Example 1

10 Samples of clean, distilled water were out-gassed by a process of repeated freezing in liquid nitrogen, followed by pumping down to a pressure of 0.01mbar and then melting in a sealed tube. The dissolved gas produced on each melting cycle was removed on re-freezing. Although this process was carried out five times, typically no further de-gassing on melting was observed after 3-4 cycles. The vacuum pressure of 0.01mbar corresponds to a de-gassing level of about 99.999%.

15 This water was then used to clean strips of standard filter paper having finely divided activated charcoal rubbed into their surface to produce a uniform blackened region, by placing each strip into a respective test tube and pouring the water into the tube. The cleaning effect of the de-gassed water was compared with that of distilled water that had not been de-gassed.

20

In Figure 2a the left-hand tube contains the de-gassed water and the right-hand tube the non de-gassed distilled water. In both cases the same volume of water was simply poured onto the dirty paper.

25 In Figure 2b the left-hand tube contains the non de-gassed distilled water and the right-hand tube the de-gassed water. In both cases the same volume of water was poured onto the dirty paper and then the tubes with the strips immersed in the water were vigorously shaken by hand for 8 seconds.

30 In both of these rudimentary, non-optimum, cleaning experiments it was immediately obvious from visual examination that the de-gassed water removed substantially

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greater amounts of the activated charcoal. In the experiment whose results are illustrated in Figure 2a, in pouring the de-gassed water it was clear that some areas were being cleaned and a significant amount of fine carbon was carried to the surface. By comparison, in the experiment whose results are illustrated in Figure 2b, on shaking the tube, the de-gassed water produced significantly more charcoal sediment and a more cloudy solution.

It is interesting that these simple experiments clearly indicate that de-gassed water does have an improved cleaning effect because the substrate in this case, paper, is hydrophilic and finely divided activated charcoal is, in any case, fairly easily dispersed in normal, gassed water.

Example 2

In this example, a small amount of the hydrocarbon oil dodecane was left in the base of each of two glass tubes. The same volume of normal water that had not been de-gassed and water that had been de-gassed in the manner described in Example 1 was poured into respective tubes and the tubes were shaken vigorously for 8 seconds.

Figure 3 shows the turbidity of the water in each tube for five minutes after this procedure. The results clearly demonstrate that de-gassed water is more effective at removing residual oil 'dirt' on glass. These results are particularly interesting and important because the oil was completely equilibrated with the atmosphere prior to cleaning and hence contained dissolved gas at a significantly higher level than even the normal water. The diffusion of dissolved gas from the oil does not appear to prevent the cleaning enhancement of de-gassed water. Presumably this is rate dependent and rapid cleaning will favour the enhancement using de-gassed water.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications

which fall within its spirit and scope. The invention also includes all the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

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Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step
30 or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

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The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in Australia.

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Dated this 23rd day of December 2003

The Australian National University

By Its Patent Attorneys

10 **DAVIES COLLISON CAVE**

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%De-gassed vs vacuum pressure

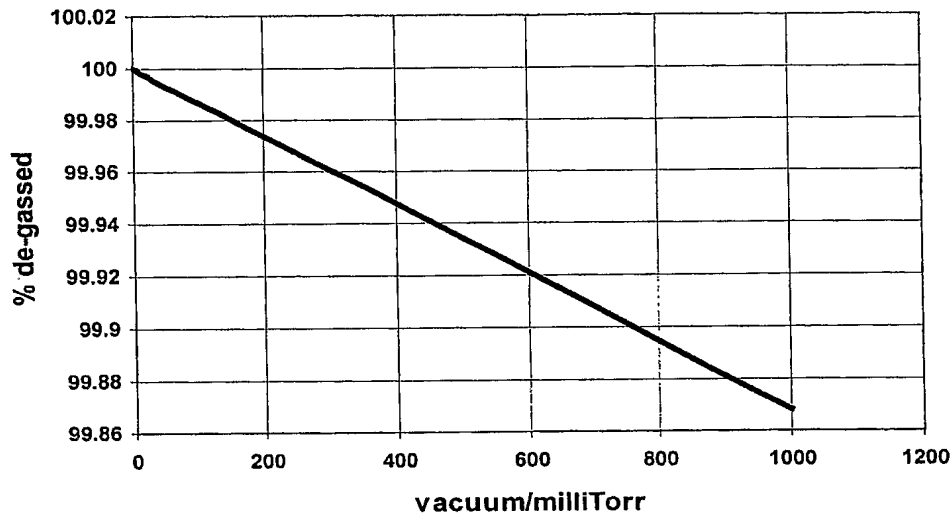


Figure 1

Turbidity of cleaning water

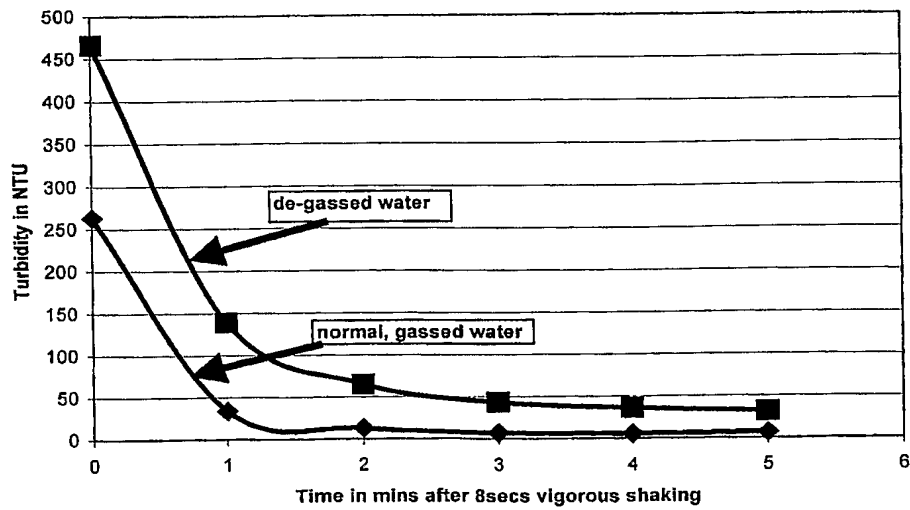


Figure 3

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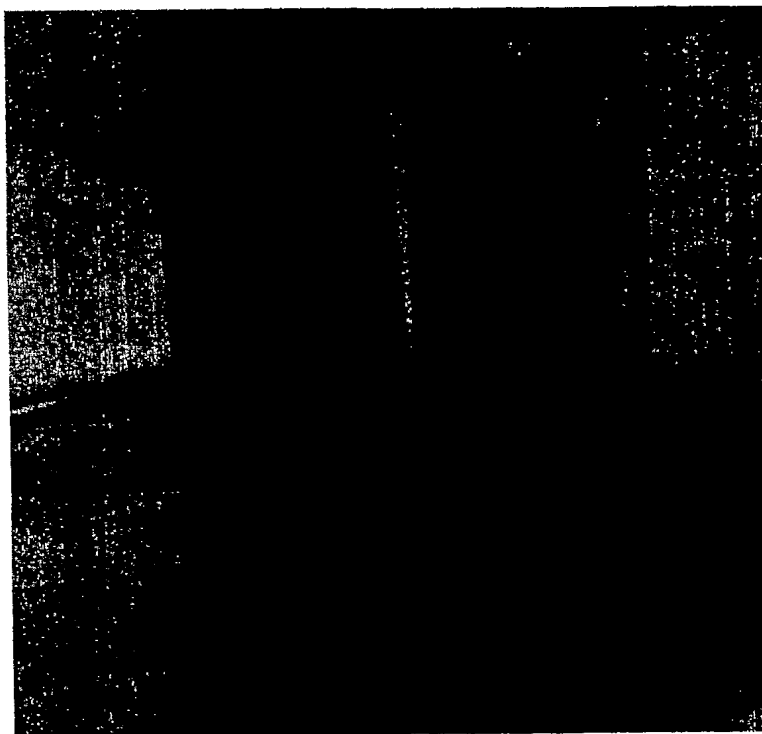


Figure 2a

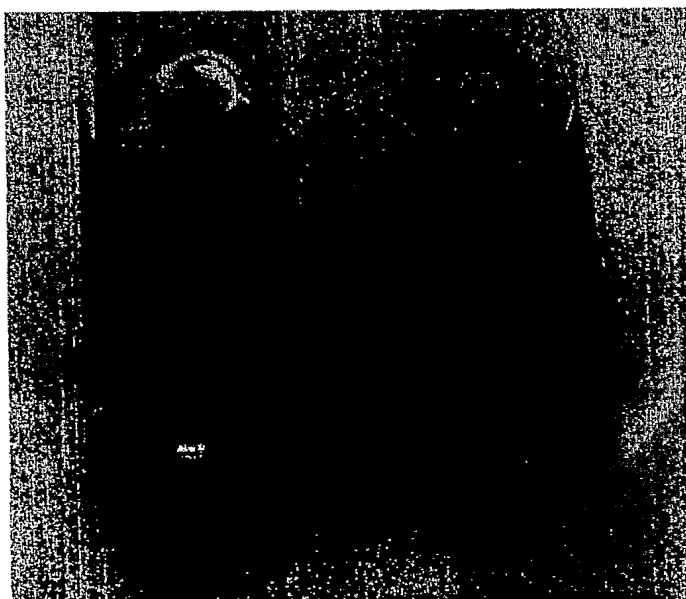


Figure 2b